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Ionic Liquid-Based Microemulsions in Catalysis

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Supporting Information

ABSTRACT: The design and properties of surface-active ionic liquids that are able to form stable microemulsions with heptane and water are presented, and their promise as reaction media for thermomorphic palladium-catalyzed cross-coupling reactions is demonstrated.



INTRODUCTION

Microemulsions are thermodynamically stable, isotropic, optically transparent solutions composed of two intrinsically immiscible solvents in the presence of one or more surfactants, and have found wide application for catalytic reactions and processes.^{1,2} They are particularly suitable as nanoreactors for many catalytic transformations due to their microstructure, which may vary continuously from spherical to cylindrical, tubular, and bicontinuous oil and water phases.³ The nanometer-sized oil or water droplets provide highly dynamic nanoreactors, with the interface disintegrating and reforming on a time scale of milliseconds, which can promote favorable reaction kinetics.⁴ Moreover, microemulsions can simultaneously co-solubilize large volumes of hydrophilic and hydrophobic compounds, which can overcome the solubilization barriers of the formerly immiscible liquids.

The formation of stable microemulsions between two intrinsically immiscible liquids, e.g., oil and water, requires the presence of amphiphiles to reduce the interfacial tension between the two phases to a very low value. However, microemulsions must not necessarily consist of organic solvents and water, alternative fluids such as ionic liquids have been investigated.⁵ Different concepts can be, and have been, realized in this regard, including mostly nonaqueous microemulsions, where water is replaced with room-temperature ionic liquids, for example in the well-studied system {1-butyl-3-methylimidazolium tetrafluoroborate, [C₄mim][BF₄]/toluene/Triton X-100}.⁶ Other examples include water–ionic liquid microemulsions, e.g., {H₂O/1-butyl-3-methylimidazolium hexafluorophosphate, [C₄mim][PF₆]/Triton X-100},^{7–9} or even a

microemulsion of two intrinsically immiscible ionic liquids, e.g., 1-octylimidazolium aprotic and protic ionic liquids with the anionic surfactant, 1,4-bis[(2-ethylhexyl)oxy]-1,4-dioxobutane-2-sulfonate (commonly known as docusate or [AOT][–])¹⁰—all of them stabilized by the addition of one or more conventional surfactants. Less attention has been focused on the use of ionic liquids as amphiphiles themselves, and only a few examples exist where surface-active ionic liquids are used to reduce the interfacial tension of two immiscible solvents to form stable microemulsions.¹¹ This is surprising, as the surfactant behavior is a natural consequence of the structure of ionic liquids featuring cations with a hydrophilic headgroup and a hydrophobic tail, i.e., the alkyl chain attached to the ions.^{12,13} More recently, the properties of catanionic ionic liquids, containing both anions and cations with hydrophobic tails, have proved to be exceptional.^{14,15} Surface-active ionic liquids have already been well explored for a number of applications in synthesis,^{16,17} catalysis^{18,19} and separations^{20,21} rendering them ideally suited for the development of targeted microemulsions,^{22–26} and for their separation.²⁷

In this article, the design and synthesis of surface-active ionic liquids composed of both surface-active cations and anions that are capable of forming stable microemulsions with heptane and water are reported. These microemulsions were applied as reaction media for palladium-catalyzed Suzuki cross-coupling reactions, resulting in high reactivity even at low catalyst

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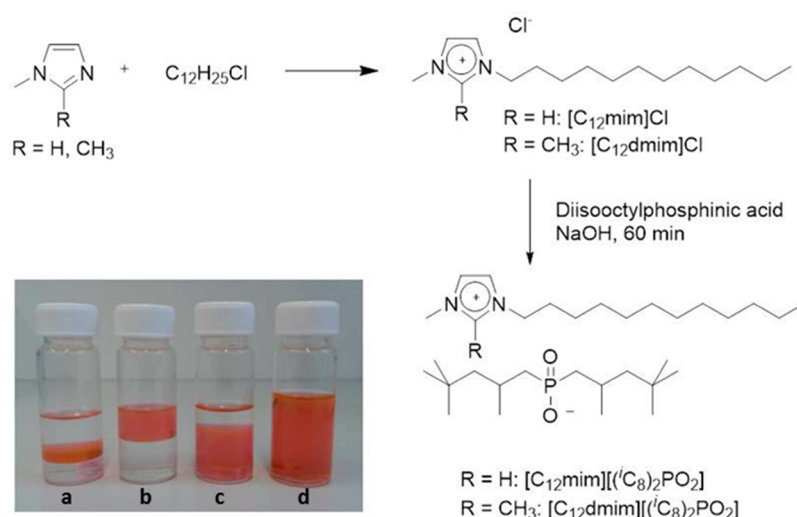


Figure 1. Preparation of phosphinate ionic liquids with surface-active cations. The picture inset shows mixtures of heptane/water/ $[\text{C}_{12}\text{mim}][(\text{C}_8\text{H}_{17})_2\text{PO}_2]$ in various compositions (a:0.5/0.4/0.1, b:0.5/0.3/0.2, c:0.1/0.7/0.2 and d:0.2/0.4/0.4 wt. /g), colored with the dye, eosin.

loadings, with simple product separation and successful catalyst recycling through thermomorphic catalysis.

RESULTS AND DISCUSSION

Ionic Liquid Synthesis. Our strategy for the preparation of ionic liquid-based stable microemulsions relied on the design of ionic liquids that are composed of surface-active imidazolium cations in combination with a dialkylphosphinate anion.

As it is well-known that imidazolium cations are far from innocent when used in transition metal catalysis, we selected two surface-active ionic liquids, namely $[\text{C}_{12}\text{mim}][(\text{C}_8\text{H}_{17})_2\text{PO}_2]$ and $[\text{C}_{12}\text{dmim}][(\text{C}_8\text{H}_{17})_2\text{PO}_2]$, for this study (Figure 1). Both ionic liquids were prepared according to the standard alkylation-metathesis methodologies in two-steps, initially providing the surface-active chloride ionic liquids $[\text{C}_{12}\text{mim}]\text{Cl}$ and $[\text{C}_{12}\text{dmim}]\text{Cl}$.²⁸ The metathesis with the surface-active anion was performed with the sodium salt of bis(2,4,4-trimethylpentyl)phosphinic acid, a cheap mining chemical sold under the brand name Cyanex 272.²⁹ As the prepared hydrophobic ionic liquids naturally tend to form emulsions, workup and purification after ion exchange was difficult and required the formation of a three-phase system after addition of water and hexane, with the aid of ethanol. This strategy allowed the repeated extraction of the ionic liquids with water to reduce the chloride content, and both ionic liquids were isolated with good purity and yields of 86 and 88%, respectively. Based on their dual surfactant nature, these ionic liquids have the ability to bring hydrophobic and hydrophilic solvents together as stable microemulsions that can form multiphase system phases (Figure 1, inset).

Phase Behavior. Detailed investigations on the phase behavior of water-heptane-ionic liquid mixtures at 25 °C via titration and conductivity measurements showed that all four types of Winsor microemulsion systems are present in the ternary phase diagram for the surface-active ionic liquid $[\text{C}_{12}\text{mim}][(\text{C}_8\text{H}_{17})_2\text{PO}_2]$, indicating the typical phase behavior found for many mixtures of oil (here heptane), water, and ionic surfactants at variable salinity (Figure 2).^{30–32} According to the Winsor classification, there are four general types of microemulsion systems: At small concentration of a surfactant biphasic system of oil-in-water (o/w) microemulsions form

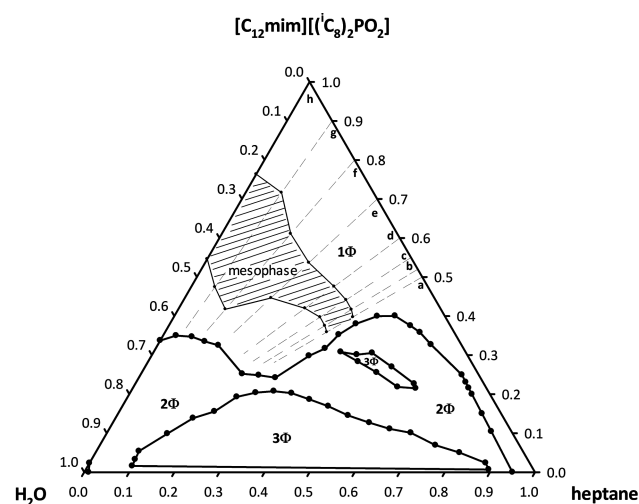


Figure 2. Ternary phase diagram of the system heptane/water/ $[\text{C}_{12}\text{mim}][(\text{C}_8\text{H}_{17})_2\text{PO}_2]$ at 25 °C. 1Φ denotes a single phase system (Winsor IV), 2Φ corresponds to a biphasic system with oil-in-water (o/w) microemulsions with an excess of oil (Winsor I) or water-in-oil (w/o) microemulsions with an excess of water (Winsor II), and 3Φ denotes a triphasic area with a surfactant-rich middle-phase (Winsor III). Letters a–h correspond to the starting points for conductivity studies as a function of water content.

with excess oil can be formed (Winsor I). Alternatively, the ionic liquid-rich water-in-oil (w/o) microemulsion may coexist with the ionic liquid-poor aqueous phase (Winsor II). Type III corresponds to a three-phase system where an ionic liquid-rich middle-phase coexists with both excess water and oil ionic liquid-poor phases (Winsor III), while Winsor type 4 is a single-phase isotropic solution which forms upon addition of higher amount of ionic liquid (Winsor IV).³³

Interestingly, the two-phase o/w microemulsion system (Winsor I) is interrupted by a small and isolated three-phase system with a bicontinuous middle phase (Winsor III). Moreover, a gelatin mesophase was identified via conductivity measurements carried out in order to study the microstructural transformations from a droplet microemulsion to a bicontinuous phase. Based on percolation theory, Clause et al.³⁴ have identified different types of microemulsions, i.e., water-in-oil,

oil-in-water, and bicontinuous microemulsions via conductivity measurements in the optically clear phase region at variable water content. The variation of conductivity as a function of water content was further studied and gave information on the microstructural transformations from a droplet microemulsion to a bicontinuous phase. With increasing water content, the initial nonlinear increase of conductivity indicates the existence of a percolation phenomenon that is attributed to inverse microdroplet aggregation, while the following linear increase is due to the formation of a w/o microemulsion.³⁵ At a certain water concentration, a sharp decrease in conductivity indicates the formation of a bicontinuous mesophase (see Figure 3).

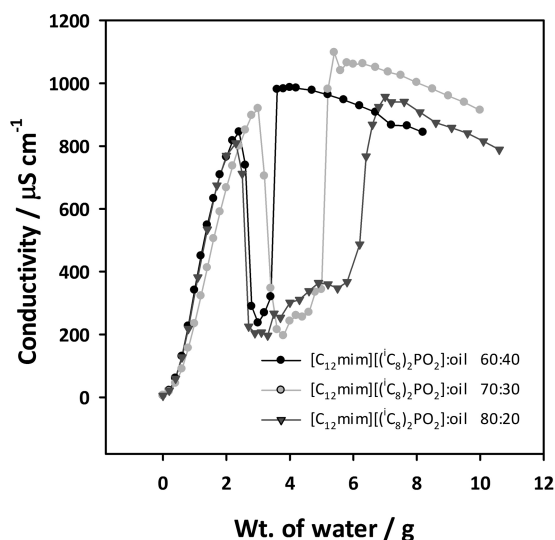


Figure 3. Electric conductivity of $[C_{12}mim][(C_8H_{17})_2PO_2]$ microemulsion solutions as a function of water content, with 60, 70, and 80% $[C_{12}mim][(C_8H_{17})_2PO_2]$, corresponding to the starting points d, e, and f in the phase diagram.

Catalytic Studies. After evaluation of suitable phase behavior, the application of these novel ionic liquid based microemulsions as reaction media was studied in palladium-catalyzed cross-coupling processes that are widely used in the pharmaceutical industry for C–C bond formation.³⁶ The chosen Suzuki reaction, a cross-coupling reaction between aryl halides with boronic acids,³⁷ typically leads to the formation of substituted biaryl moieties that are present in many pharmaceutically active compounds, herbicides, new materials, polymers, liquid crystals, and ligands.³⁸ Despite extensive work and progress in ligand and catalyst design, the product separation and catalyst recovery can still provide an obstacle for large scale processing. Recent trends in this area have addressed the application of thermomorphic catalysis for this purpose, relying on temperature-dependent phase behavior for catalyst recycling, as shown in an elegant study by Schomäcker and co-workers.³⁹ Here, the palladium-catalyzed Suzuki cross-coupling reaction between 4-bromoacetophenone and phenyl boronic acid was selected to evaluate the application of ionic liquid-based microemulsions as reaction media for transition metal catalysis (Figure 4).

Initially, the optimization of reaction conditions for this model reaction was done with respect to base and catalyst loading (Table 1, entries 1–5). With the aid of the ternary phase diagram (Figure 2), further variations of ionic liquid/heptane/water ratios in the three phase region (Winsor III)

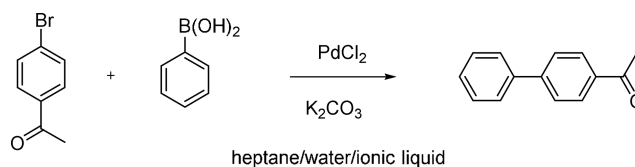


Figure 4. Suzuki coupling reaction of 4-bromoacetophenone and phenylboronic acid in ionic liquid based microemulsions.

allowed identification of suitable reaction conditions. The compositions of these microemulsions are conveniently characterized by parameters α and γ :²

$$\alpha = \frac{m_{\text{oil}}}{(m_{\text{oil}} + m_{\text{water}})} \quad (1)$$

$$\gamma = \frac{m_{\text{IL}}}{(m_{\text{oil}} + m_{\text{water}} + m_{\text{IL}})} \quad (2)$$

Interestingly, the best yields under standard conditions (entries 7 and 9) correspond to largest values of γ with the smallest values of α . If this proves to be a general observation, it will lend itself to design experiment optimizations⁴⁰ of catalytic systems with microemulsions. For both ionic liquids $[C_{12}mim]-(C_8H_{17})_2PO_2$ and $[C_{12}dmim]-(C_8H_{17})_2PO_2$, a decrease in the amount of heptane—corresponding to a lower α value of 0.375—results in higher yield (Table 1, entry 7). On the contrast, a decrease in the water content, i.e., a change from $\alpha = 0.5$ to $\alpha = 0.625$ did not alter the yield significantly. Eventually, complete conversion and quantitative yield of 4-ethanoylbi-phenyl was obtained for both ionic liquids $[C_{12}mim]-(C_8H_{17})_2PO_2$ and $[C_{12}dmim]-(C_8H_{17})_2PO_2$ at optimized conditions (IL/heptane/ H_2O 0.1/0.6/1, 0.18 mmol K_2CO_3) in short reaction times (1 h) at a low catalyst loading of 0.1 mol% $PdCl_2$.

As can be seen from Table 1, the yield of the reaction without ionic liquid in a simple biphasic mixture is around 70% (entry 12). The addition of a small amount of ionic liquid renders the biphasic mixture into a stable triphasic system with an intermediate microemulsion layer (Winsor III), which results in increased yields. In fact, the formation of the nanoreactors in the microemulsion where a polar reagent reacts with an oily substrate is a clear advantage, and results in high reactivity, even at room temperature (entry 8). The impact of microemulsion formation is also visible when comparing results in pure ionic liquid, pure heptane or pure water (entries 13–15). Yields of the Suzuki reaction performed in a single solvent remained drastically below the results obtained with the microemulsion system; in fact no conversion was observed when the reaction as performed in the pure ionic liquid $[C_{12}mim]-(C_8H_{17})_2PO_2$ (entry 15). Eventually, a control experiment was performed in the presence of 0.01 mmol bis(2,4,4-trimethylpentyl)phosphinic acid, as it is well-known that phosphinates can act as P,O ligands for palladium (entry 16).⁴¹ While a good yield of 86% could be obtained with 10 mol% bis(2,4,4-trimethylpentyl)phosphinic acid, the values remained clearly below the yields obtained in the microemulsion system, thereby emphasizing the high reactivity obtained in the ionic liquid/heptane/ H_2O microemulsion system.

Although both ionic liquids were able to form microemulsions, and are suitable reaction media for the chosen Suzuki reaction, $[C_{12}mim]-(C_8H_{17})_2PO_2$ and $[C_{12}dmim]-(C_8H_{17})_2PO_2$ showed entirely different behavior during the

Table 1. Optimisation of Reaction Conditions for the Suzuki Reaction between 4-Bromoacetophenone and Phenyl Boronic Acid

entry ^a	ionic liquid	weight ratio IL/heptane/H ₂ O	α	γ	Base/mmol	catalyst/ mol%	yield/ % ^c
1	[C ₁₂ mim][(ⁱ C ₈) ₂ PO ₂]	0.1/1/1	0.5	0.048	0.10	0.1	78
2	[C ₁₂ mim][(ⁱ C ₈) ₂ PO ₂]	0.1/1/1	0.5	0.048	0.15	0.1	92
3	[C ₁₂ mim][(ⁱ C ₈) ₂ PO ₂]	0.1/1/1	0.5	0.048	0.18	0.1	95
4	[C ₁₂ mim][(ⁱ C ₈) ₂ PO ₂]	0.1/1/1	0.5	0.048	0.18	0.075	80
5	[C ₁₂ mim][(ⁱ C ₈) ₂ PO ₂]	0.1/1/1	0.5	0.048	0.18	0.005	67
6	[C ₁₂ mim][(ⁱ C ₈) ₂ PO ₂]	0.1/1/0.6	0.625	0.059	0.18	0.1	88
7	[C ₁₂ mim][(ⁱ C ₈) ₂ PO ₂]	0.1/0.6/1	0.375	0.059	0.18	0.1	> 99
8	[C ₁₂ mim][(ⁱ C ₈) ₂ PO ₂]	0.1/0.6/1	0.375	0.059	0.18	0.1	> 99 ^b
9	[C ₁₂ dmim][(ⁱ C ₈) ₂ PO ₂]	0.1/1/1	0.5	0.048	0.18	0.1	95
10	[C ₁₂ dmim][(ⁱ C ₈) ₂ PO ₂]	0.1/0.6/1	0.375	0.059	0.18	0.1	> 99
11	[C ₁₂ dmim][(ⁱ C ₈) ₂ PO ₂]	0.1/1/0.6	0.625	0.059	0.18	0.1	94
12	[C ₁₂ mim][(ⁱ C ₈) ₂ PO ₂]	0/1/1	0.5	0	0.18	0.1	70
13	[C ₁₂ mim][(ⁱ C ₈) ₂ PO ₂]	1/0/0	0	1	0.18	0.1	< 1
14		0/1/0	1	0	0.18	0.1	42
15		0/0/1	0	0	0.18	0.1	78
16		0/0.6/1	0.375	0	0.18	0.1	86 ^c

^aPerformed with 0.1 mmol 4-bromoacetophenone, 0.15 mmol phenyl boronic acid, and 0.0001 mmol (0.1 mol%) PdCl₂ at 80 °C unless otherwise indicated. Yield determined by HPLC using ethyl benzoate as internal standard. ^bPerformed at 25 °C. ^cPerformed with 0.01 mmol bis(2,4,4-trimethylpentyl)phosphinic acid as additive.

reaction. The presence of an acidic proton, H(2), in the 1,3-dialkylimidazolium system enables ionic liquids, such as [C₁₂mim][(ⁱC₈)₂PO₂], to act as electron-rich, neutral σ -donor ligands in *N*-heterocyclic carbene (NHC)⁴² complexes with various transition metals.⁴³ In fact, NMR studies on ionic liquid based microemulsions clearly showed the presence of Pd-NHC carbene complexes in the presence of PdCl₂ in the microemulsions composed of [C₁₂mim][(ⁱC₈)₂PO₂]. A sample taken from the heptane layer showed, after evaporation of volatiles, the characteristic ¹³C NMR signal of the carbene carbon atom at ca. 210 ppm, indicating strong electron donation from the metal to the carbene ligand (Figure 5).

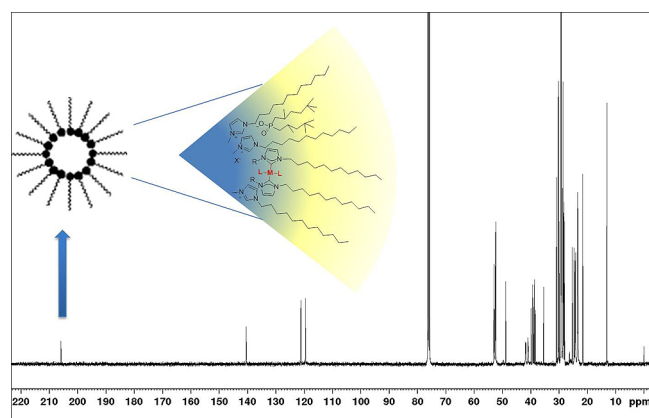


Figure 5. ¹³C NMR spectrum of top oil phase of heptane/water/[C₁₂mim][(ⁱC₈)₂PO₂] microemulsions showing NHC carbene complex formation between the ionic liquid and PdCl₂.

These findings demonstrate that the role of ionic liquid is not limited to the formation of a suitable reaction media. Instead, [C₁₂mim][(ⁱC₈)₂PO₂] plays a dual role of surfactant and ligand, resulting in the outstanding reactivity even at room temperature. In case of [C₁₂dmim][(ⁱC₈)₂PO₂], NHC complex formation between ionic liquid and palladium is clearly impossible, since the C(2) position is blocked with the bulky

methyl group. In contrast, we observed the formation of finely dispersed palladium nanoparticles during the reaction that are well stabilized and immobilized in the intermediate microemulsion phase as proven with TEM images (see Figure 6). A

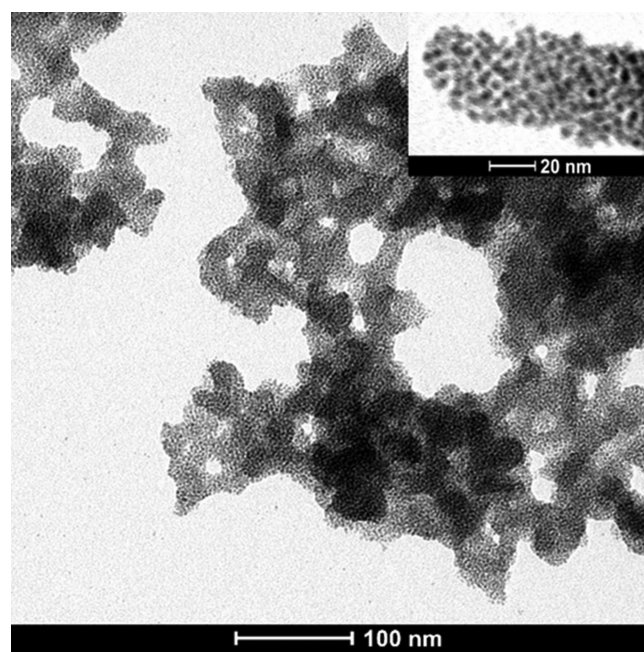


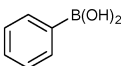

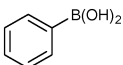
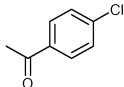
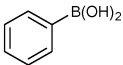
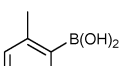
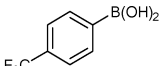
Figure 6. TEM image of palladium nanoparticles from the intermediate microemulsion phase, [C₁₂dmim][(ⁱC₈)₂PO₂].

similar effect was reported by Zhang et al.⁷ who used the H₂O/TX-100/1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim]PF₆) microemulsions as a medium for the in situ preparation of Pd nanoparticles, and several studies in literature focused on the application of Pd nanoparticles in microemulsion as efficient catalytic system for cross-coupling reactions.^{44–46}

Based on the optimized conditions (α and γ of 0.375 and 0.059, respectively), the substrate scope was expanded to

include various substituted starting materials with both electron-withdrawing and electron-donating functionalities (Table 2). Excellent isolated yields >90% were obtained for

Table 2. Scope and Limitations of Palladium-Catalysed Suzuki Cross-Coupling with a Variety of Boronic Acid and a Range of Aryl Halides, Using Ionic Liquid-Based Microemulsions^a

Aryl halide	Boronic acid	Isolated yield /%
-COCH ₃		99
-CF ₃		99
-NO ₂		97
-CN		94
-OH		82
-CH ₃		50 ^b
-OCH ₃		45 ^b
		23
		9
-COCH ₃		7
-NO ₂		8
-COCH ₃		100
-NO ₂		83

^aReaction conditions: [C₁₂dmim][(C₈)₂PO₂]/heptane/H₂O 0.1:0.6:1.0 g, PdCl₂ 0.1 mol%, K₂CO₃ 0.18 mmol, boronic acids 0.15 mmol, aryl halides 0.1 mmol, temperature 80 °C, time 60 min.

^bYield determined by GC.

most products with aryl halides or boronic acids with electron-deficient substituents, which is in accordance with literature data for Suzuki couplings. Moreover, the products could be directly isolated by crystallization from the heptane phase. However, in the cases of less reactive chloroarenes, or sterically demanding starting materials, such as 2,6-dimethylbromobenzene or 2,6-dimethylphenylboronic acid, yields remained below expectation. The catalytic system seems to be less effective in C–C bond formation of chloroarenes, indicating that their conversion in Suzuki cross coupling is still a challenge.

The preferential solubility of the starting materials, products and catalysts in different microemulsion layers, in combination with the temperature-dependent phase behavior, offers novel opportunities for catalyst recycling.⁴⁷ In the chosen reactions, phenylboronic acid and base are soluble in the lower aqueous phase, bromoacetophenone or the product 4-acetylbiphenyl is dissolved in the top heptane phase, whereas the transition metal catalyst—either in a well-defined molecular state, or as a nanoparticle dispersion—is preferentially located in the intermediate bicontinuous microemulsion layer (Figure 7).

The strategy outlined here for thermomorphic catalysis with catalyst recovery relies on a stepwise shift of phase boundaries. Initially, the triphasic microemulsion system is charged with catalyst and starting materials at room temperature. An increase in reaction temperature to 80 °C results in a shift of phase boundaries to two phases, while, in case of [C₁₂dmim]–[(C₈)₂PO₂], well-dispersed palladium nanoparticles are simultaneously formed. Once complete conversion is reached, the reaction is cooled to 60 °C, resulting in the reformation into a stable triphasic system. At this lower temperature, the top organic layer can easily be separated. Eventually, the product crystallizes from the separated heptane phase at room temperature and can be easily isolated by filtration as colorless crystals in high purity.

Simultaneously, salts formed during the reaction can be removed with the aqueous phase, while the catalyst remains immobilized in the ionic liquid-rich middle phase. A consecutive run can then be started by addition of fresh starting materials and solvents, i.e., 4-bromoacetophenone, phenyl boronic acid, base, heptane, and water.

Again, considerable differences in catalyst recovery were found for the two ionic liquids. In the case of [C₁₂mim]–[(C₈)₂PO₂], considerable leaching of the palladium catalyst—probably in its NHC complex form—into the top heptane layer was observed, resulting in contamination of the crude product. Consequently, yields decrease drastically in the first three runs due to both catalyst and ionic liquid losses. In contrast, catalyst leaching was not an issue with microemulsions composed of [C₁₂dmim][(C₈)₂PO₂]. As shown in Table 3, the same batch of [C₁₂dmim][(C₈)₂PO₂] and catalyst were run consecutively for five times with no significant loss in performance. Although traces of ionic liquid were found in the product after the third run, this did not affect the catalytic performance, and a yield >90% could be isolated from [C₁₂dmim][(C₈)₂PO₂].

CONCLUSIONS

The design of novel surface-active ionic liquids that are able to form stable microemulsions systems has been achieved, and their application as novel reaction media for transition metal catalysis has been demonstrated. High reactivity was observed even at low catalyst loadings, while the temperature-dependent phase behavior allowed simple product separation and successful catalyst recycling through thermomorphic catalysis. While more investigations of the microemulsion nanostructure are clearly required, and currently under way, a fundamental difference was found between carbene- and noncarbene forming ionic liquids, suggesting that the ionic liquid can play a dual role as surfactant and ligand. The exploitation of these tailor-made microemulsion systems for a number of transition metal catalyzed reactions, and also their application in multiple separation problems, are currently ongoing in our laboratories.

EXPERIMENTAL SECTION

Commercially available reagents and solvents were used, as received without further purification, unless otherwise specified. All ionic liquids were dried for at least 24–48 h at room temperature or 50 °C and 0.01 mbar before use.

¹H and ¹³C NMR spectra were recorded on a 400 MHz spectrometer using the solvent peak as reference, and heteronuclear single quantum coherence experiments (HSQC) were used to confirm the peak assignments. Infrared spectra were recorded on a FT IR spectrometer equipped with a single reflection ATR unit. TEM studies were performed on a transmission electron microscope operating at 160 kV. The samples for TEM studies were prepared by precipitation

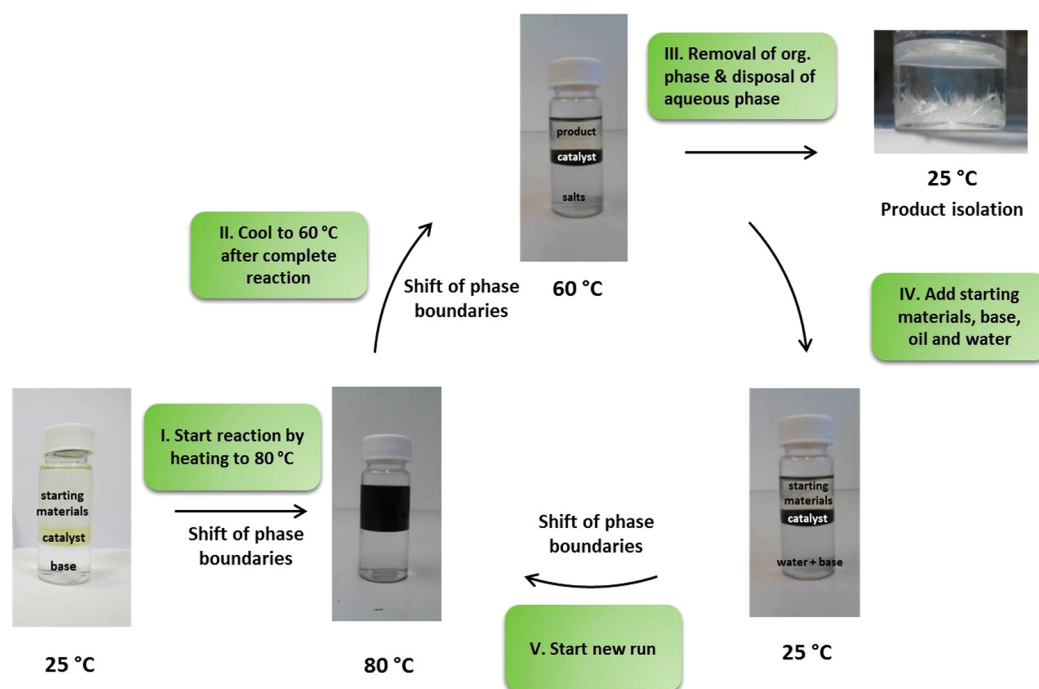


Figure 7. Recycling strategy for thermomorphic Suzuki coupling reaction in $[\text{C}_{12}\text{dmim}][(\text{C}_8)_2\text{PO}_2]$ relying on a temperature dependent multicomponent solvent system.

Table 3. Catalyst Recycling in the Suzuki Reaction between 4-Bromoacetophenone and Phenyl Boronic Acid in the Presence of Ionic Liquids $[\text{C}_{12}\text{mim}][(\text{C}_8)_2\text{PO}_2]$ and $[\text{C}_{12}\text{dmim}][(\text{C}_8)_2\text{PO}_2]$ ^a

run ^a	$[\text{C}_{12}\text{mim}][(\text{C}_8)_2\text{PO}_2]$ yield/% ^b	$[\text{C}_{12}\text{dmim}][(\text{C}_8)_2\text{PO}_2]$ yield/% ^b
1	> 99 ^c	98
2	80 ^c	99
3	60 ^c	97 ^c
4	n.d.	95 ^c
5	n.d.	91 ^c

^aPerformed with 1 mmol 4-bromoacetophenone, 1.5 mmol phenyl boronic acid, and 0.001 mmol (0.1 mol%) PdCl_2 at 80 °C for 1 h.

^bIsolated yield after direct crystallization from heptane phase. ^cIsolated yield after recrystallization from heptane. n.d.; not determined.

of the nanoparticles in ethanol, centrifuged (13 000 rpm), and redispersed in ethanol. A drop of the dispersion (3 μL) was added on a 300-mesh carbon-coated copper grids and the solvent was subsequently evaporated in air.

HPLC analysis was performed on a HPLC unit equipped with a PDA detector under reverse-phase conditions. A reversed phase C18 column (250 \times 4.6, 5 μm) was used with $\text{MeOH}:\text{H}_2\text{O}$ (70:30; 0.1% trifluoroacetic acid) as solvent and a flow of 0.8 $\text{cm}^3 \text{min}^{-1}$; detection was at 210 nm, at 30 °C column oven temperature and ethyl benzoate as internal standard. Calibration curves were prepared in the range from 2.0 to 0.01 mg cm^{-3} for starting materials and products.

Ternary phase diagrams were investigated at 25 °C for $\{[\text{C}_{12}\text{mim}][(\text{C}_8)_2\text{PO}_2]:\text{water}:\text{heptane}\}$, where $[\text{C}_{12}\text{mim}]^+$ is 1-dodecyl-3-methylimidazolium, and $(\text{C}_8)_2\text{P}(\text{O})\text{OH}$ is bis(2,4,4-trimethylpentyl)-phosphinic acid. The isotropic phase was determined by visual inspection titration of the water:heptane mixture (at different ratios) with $[\text{C}_{12}\text{mim}][(\text{C}_8)_2\text{PO}_2]$ at 25 °C. After adding each drop, the mixture was stirred and left to equilibrate for appropriate times until clear phases were obtained. Conductivity measurements (equilibrated at 25 °C) were carried out in order to study the microstructural transformations from a droplet microemulsion to a bicontinuous phase for one phase area at different ratios of $[\text{C}_{12}\text{mim}][(\text{C}_8)_2\text{PO}_2]:\text{heptane}$

(50–100% of ionic liquid). After each water addition, but before each final measurement, the mixture was mixed until stable conductivity measurements were achieved.

■ SYNTHETIC PROCEDURES

Precursor Chloride Ionic Liquids. The chloride imidazolium salts were synthesized according to standard methodologies,⁴⁸ but which have not been detailed previously.

1-Dodecyl-3-methylimidazolium Chloride, $[\text{C}_{12}\text{mim}]\text{Cl}$. A mixture of 1-methylimidazole (99%; 30.0 g, 0.37 mol) and 1-chlorododecane (97%; 82.3 g, 0.40 mol) was heated with an oil bath at 100 °C in a three-neck round-bottomed flask (250 cm^3) equipped with a stirrer bar and reflux condenser, under a dry argon atmosphere for 72 h. The crude product (a viscous yellow liquid) was repeatedly recrystallized from anhydrous tetrahydrofuran, to eventually give colorless crystals (yield: 97%; mp 45–46 °C). ¹H NMR (400 MHz; CDCl_3 ; 22 °C): δ/ppm = 0.83 (3H, t, $\text{NC}_{11}\text{H}_{22}\text{CH}_3$, J = 6.36 Hz), 1.20 (18H, m, $\text{C}_9\text{H}_{18}\text{CH}_3$), 1.86 (2H, m, NCH_2CH_2), 4.09 (3H, s, NCH_3), 4.27 (2H, t, NCH_2 , J = 14.83 Hz), 7.35 (1H, s, H(4)-im), 7.54 (1H, s, H(5)-im), 10.57 (1H, s, H(2)-im). ¹³C NMR (100 MHz; CDCl_3 ; 22 °C): δ/ppm = 137.4 (d, C(2)-im), 123.8 (d, C(5)-im), 121.8 (d, C(4)-im), 49.8 (t, NCH_2), 36.4 (q, NCH_3), 26.1–31.7 (t, $\text{C}_8\text{H}_{16}\text{CH}_2\text{CH}_3$), 22.5 (t, NCH_2CH_2), 13.9 (q, CH_3).

1-Dodecyl-2,3-dimethylimidazolium Chloride, $[\text{C}_{12}\text{dmim}]\text{Cl}$. The synthesis was analogous to that of $[\text{C}_{12}\text{mim}]\text{Cl}$, except that the amine used was 1,2-dimethylimidazole (98%; 35.6 g, 0.37 mol), giving colorless crystals (yield: 80%; mp 89–90 °C). ¹H NMR (400 MHz; CDCl_3 ; 22 °C): δ/ppm = 0.74 (3H, t, $\text{NC}_{11}\text{H}_{22}\text{CH}_3$, J = 6.86 Hz), 1.11 (18H, m, $\text{CH}_2\text{C}_9\text{H}_{18}\text{CH}_3$), 1.67 (2H, m, NCH_2CH_2), 2.70 (3H, s, $-\text{CCH}_3$), 3.93 (3H, s, NCH_3), 4.10 (2H, t, NCH_2 , J = 14.88 Hz), 7.44 (1H, d, H(4)-im, J = 2.04 Hz), 7.78 (1H, d, H(5)-im, J = 2.08 Hz). ¹³C NMR (100 MHz; CDCl_3 ; 22 °C): δ/ppm = 143.4 (d, C(2)-im), 123.3 (d, C(5)-im), 121.4 (d, C(4)-im), 49.8 (t, NCH_2), 35.9 (q, NCH_3), 26.4–31.8 (t, $\text{C}_8\text{H}_{16}\text{CH}_2\text{CH}_3$), 22.6 (t, NCH_2CH_2), 14.0 (q, CH_3), 10.5 (q, CH_3).

Phosphinate Ionic Liquids. 1-Dodecyl-3-methylimidazolium Bis(2,4,4-trimethylpentyl)phosphinate, $[\text{C}_{12}\text{mim}][(\text{C}_8)_2\text{PO}_2]$. Bis-(2,4,4-trimethylpentyl)phosphinic acid (90%; 22.28 g, 0.077 mol) and sodium hydroxide (30.0 g, 0.077 mol) were dissolved in distilled

water (150 cm³). A solution of [C₁₂mim]Cl (20.0 g, 0.070 mol) in distilled water (200 cm³) was added and the mixture was stirred at room temperature for 1 h. The resulting emulsion was extracted repeatedly with ethyl ethanoate. The combined organic layers were washed four times with water until no chloride was detected in the aqueous layer (AgNO₃). A three-phase washing system was used for further purification of the resulting ionic liquid. The product was purified by addition of water (150 cm³), hexane (300 cm³), and ethanol (50 cm³). The middle phase (the ionic liquid-rich phase) was separated and washed four times as above. Residual volatiles from the middle phase were removed under reduced pressure. The resultant viscous liquid was dried under high vacuum (0.01 mbar) with stirring at 50 °C for 24–48 h, to obtain a hygroscopic pale yellow viscous liquid, [C₁₂mim][C₈H₁₆PO₂] (32.6 g, 0.060 mol); yield, 86%. ¹H NMR (400 MHz; CDCl₃; 22 °C): δ/ppm = 0.77 (2H, m, CH₂CH₃, and CCH₃), 1.01 (8H, m, CCH₃, and CH₂CH₃), 1.11 (20H, m, C₈H₁₆CH₂CH₃ and CH₂C(CH₃)₃), 1.27 (2H, m, -PCH_{2,a}), 1.47 (2H, m, -PCH_{2,b}), 1.73 (2H, quin, NCH₂CH₂), 1.89 (2H, m, CH), 4.02 (3H, s, NCH₃), 4.23 (2H, t, NCH₂, J = 7.4 Hz), 7.05 (1H, s, H(4)-im), 7.13 (1H, s, H(5)-im), 11.30 (1H, s, H(2)-im). ¹³C NMR (100 MHz; CDCl₃; 22 °C): δ/ppm = 141.1 (d, C(2)-im), 122.4 (d, C(5)-im), 120.7 (d, C(4)-im), 53.9 (t, CH₂C(CH₃)₃), 49.8 (t, NCH₂), 43.3 (t, -PCH_{2,b}), 42.4 (t, -PCH_{2,a}), 36.3 (q, NCH₃), 31.8 (s, CH₂C(CH₃)₃), 31.2 (q, CH₃), 29.0–29.5 (t, C₈H₁₆CH₂CH₃), 26.3 (t, NCH₂CH₂), 25.7 (d, CH), 24.3 (q, CH₃), 22.6 (t, CH₂CH₃), 14.0 (q, CH₃). ³¹P NMR (162 MHz; CDCl₃; 22 °C) δ/ppm = 35.1 (s). FTIR, ν_{max}/cm⁻¹: 2924 and 2856 (CH), 1571 (CN-arom, CC-arom), 1467 (CH), 1164 (P = O), 1028 (P–O), 807, 658, 625. C₃₂H₆₅N₂O₂P (540.84): calcd. C 71.06, H 12.11, N 5.18, calcd. C₃₂H₆₅N₂O₂P·0.5 H₂O C 69.90, H 12.10, N 5.09, found C 69.78, H 12.10, N 5.19; residual chloride content Cl 0.041%.

1-Dodecyl-2,3-dimethylimidazolium Bis(2,4,4-trimethylpentyl)-phosphinate, [C₁₂dmim][C₈H₁₆PO₂]. The synthesis was analogous to that of [C₁₂mim][C₈H₁₆PO₂] except that [C₁₂dmim]Cl (20.8 g, 0.070 mol) was used instead of [C₁₂mim]Cl, giving a hygroscopic pale yellow viscous liquid (34.18 g, 0.062 mol); yield, 88%. ¹H NMR (400 MHz; CDCl₃; 22 °C): δ/ppm = 0.83 (2H, m, CH₂CH₃, and CCH₃), 1.05 (8H, m, CCH₃, and CH₂CH₃), 1.19 (20H, m, C₈H₁₆CH₂CH₃ and CH₂C(CH₃)₃), 1.3 (2H, m, -PCH_{2,a}), 1.48 (2H, m, -PCH_{2,b}), 1.72 (2H, quin, NCH₂CH₂), 1.91 (2H, m, CH), 2.70 (3H, s, CCH₃), 4.01 (3H, s, NCH₃), 4.08 (2H, t, NCH₂, J = 7.4 Hz), 7.39 (1H, s, H(4)-im), 8.17 (1H, s, H(5)-im). ¹³C NMR (100 MHz; CDCl₃; 22 °C): δ/ppm = 143.1 (d, C(2)-im), 124.4 (d, C(5)-im), 120.9 (d, C(4)-im), 54.0 (t, CH₂C(CH₃)₃), 48.7 (t, NCH₂), 43.4 (t, -PCH_{2,a}), 42.5 (t, -PCH_{2,b}), 35.8 (q, NCH₃), 31.8 (s, CH₂C(CH₃)₃), 31.2 (q, CH₃), 29.0–29.9 (t, C₈H₁₆CH₂CH₃), 26.4 (t, NCH₂CH₂), 25.8 (d, CH), 24.4 (q, CH₃), 22.6 (t, CH₂CH₃), 14.1 (q, CH₃), 10.1 (q, CH₃). ³¹P NMR (162 MHz; CDCl₃; 22 °C) δ/ppm = 32.9 (s). FTIR, ν_{max}/cm⁻¹: 2924 and 2856 (CH), 1541 (CN-arom, CC-arom), 1467 (CH), 1167 (P = O), 1029 (P–O), 906, 670, 631. C₃₃H₆₇N₂O₂P (554.88): calcd. C 71.43, H 12.17, N 5.05, calcd. C₃₃H₆₇N₂O₂P·2.8 H₂O C 65.48, H 12.09, N 4.63, found C 65.48, H 12.30, N 4.57, Cl 0.057. Residual chloride content Cl 0.060%.

Suzuki Reaction in Ionic Liquid-Based Microemulsions. Optimisation of Reaction Conditions. A screw-capped vial equipped with stirring bar was charged with ionic liquid [C₁₂mim][C₈H₁₆PO₂] (0.1 g), PdCl₂ (0.1 mol%), heptane (0.6 g), and water (1 g). K₂CO₃ (0.025 g, 0.18 mmol), 4-bromoacetophenone (0.020 g, 0.1 mmol), and phenylboronic acid (0.018 g, 0.15 mmol) were added and the reaction mixture was stirred in an oil bath at 80 °C for 1 h. The reaction mixture was dissolved with MeOH (50 cm³). A sample (200 μL) was taken with an Eppendorf pipet, diluted with MeOH (800 μL), and an internal standard (200 μL of ethyl benzoate in MeOH stock solution) was added. The sample was thoroughly mixed, filtered over a syringe filter (0.2 μm), and analyzed by HPLC.

General Procedure for the Suzuki Reaction. A screw-capped vial equipped with stirring bar was charged with ionic liquid [C₁₂mim][C₈H₁₆PO₂] (0.1 g), PdCl₂ (0.1 mol%), heptane (0.6 g), and water (1 g). K₂CO₃ (0.025 g, 0.18 mmol), aryl halide (0.1 mmol), and phenylboronic acid (0.018 g, 0.15 mmol) were added and the three-

phase reaction mixture was stirred in an oil bath at 80 °C for 1 h. After the reaction was complete, the vial was placed in a water bath and allowed to cool to 60 °C, resulting in the reformation of a three-phase system. At this temperature, the heptane phase was separated and left to cool to room temperature. The product crystallized directly from the heptane phase at room temperature and was isolated by filtration.

Recycling Strategy for the Thermomorphic Suzuki Reaction. A screw-cap vial was charged with ionic liquid (1 g), catalyst (0.1 mol% PdCl₂), heptane (6 g), and water (10 g). To this were added K₂CO₃ (0.25 g, 1.8 mmol), 4-bromoacetophenone (0.20 g, 1 mmol), and phenylboronic acid (0.18 g, 1.5 mmol). The mixture was magnetically stirred in an oil bath at 80 °C for 1 h, during which a shift of phase boundaries to a two-phase system was observed. The reaction vial was placed in a water bath set to 60 °C, which resulted in the formation of three phases within a minute. At this temperature, the upper heptane phase was separated to isolate the product directly. The catalyst is located in the ionic liquid-rich middle phase, which (after removing the lower water phase) remains inside the vial for the next run. Fresh heptane, water, base, and starting materials were added to the vial. The isolated yields for five runs with the same batch of microemulsion middle phase were determined.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02165.

¹H, ¹³C, ³¹P spectra of new and known compounds (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Dwars, T.; Paetzold, E.; Oehme, G. *Angew. Chem., Int. Ed.* **2005**, 44, 7174–7199.
- (2) Schwarze, M.; Pogrzeba, T.; Volovych, I.; Schomäcker, R. *Catal. Sci. Technol.* **2015**, 5, 24–33.
- (3) Olsson, U.; Wennerström, H. *Adv. Colloid Interface Sci.* **1994**, 49, 113–146.
- (4) Jiang, J.-Z.; Cai, C. J. *Colloid Interface Sci.* **2007**, 307, 300–303.
- (5) Qiu, Z.; Texter, J. *Curr. Opin. Colloid Interface Sci.* **2008**, 13, 252–262.
- (6) Gao, Y.; Wang, S.; Zheng, L.; Han, S.; Zhang, X.; Lu, D.; Yu, L.; Ji, Y.; Zhang, G. J. *Colloid Interface Sci.* **2006**, 301, 612–616.
- (7) Zhang, G.; Zhou, H.; Hu, J.; Liu, M.; Kuang, Y. *Green Chem.* **2009**, 11, 1428–1432.
- (8) Shang, W.; Kang, X.; Ning, H.; Zhang, J.; Zhang, X.; Wu, Z.; Mo, G.; Xing, X.; Han, B. *Langmuir* **2013**, 29, 13168–13174.
- (9) The use of hexafluorophosphates and tetrafluoroborates for microemulsions should be avoided, as both are readily hydrolyzed in the presence of water to generate toxic hydrogen fluoride, and contaminate the system under investigation, raising doubts about the validity of reported data. Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, 3,

- 156–164. Villagrán, C.; Banks, C.E.; Deetlefs, M.; Driver, G.; Pitner, W.R.; Compton, R.G.; Hardacre, C. Chloride Determination in Ionic Liquids. In *Ionic Liquids IIIB: Fundamentals, Progress, Challenges, and Opportunities - Transformations and Processes*. ACS Symp. Ser.; Rogers, R. D., Seddon, K. R., Eds.; American Chemical Society: Washington D.C., 2005; Vol. 902, pp 244–258.
- (10) Kusano, T.; Fujii, K.; Hashimoto, K.; Shibayama, M. *Langmuir* **2014**, *30*, 11890–11896.
- (11) Wang, S.; Zheng, Y.; Zhang, H.; Yan, Y.; Xin, X.; Yang, Y. *Ind. Eng. Chem. Res.* **2016**, *55*, 2790–2797.
- (12) Blesic, M.; Marques, M. H.; Plechkova, N. V.; Seddon, K. R.; Rebelo, L. P. N.; Lopes, A. *Green Chem.* **2007**, *9*, 481–490.
- (13) Blesic, M.; Lopes, A.; Melo, E.; Petrovski, Z.; Plechkova, N. V.; Lopes, J. N. C.; Seddon, K. R.; Rebelo, L. P. N. *J. Phys. Chem. B* **2008**, *112*, 8645–8650.
- (14) Blesic, M.; Swadźba-Kwaśny, M.; Holbrey, J. D.; Lopes, J. N. C.; Seddon, K. R.; Rebelo, L. P. N. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4260–4268.
- (15) Breen, J. M.; Olejarz, S.; Seddon, K. R. *ACS Sustainable Chem. Eng.* **2016**, *4*, 387–391.
- (16) Bica, K.; Gärtner, P.; Gritsch, P. J.; Ressmann, A. K.; Schröder, C.; Zirbs, R. *Chem. Commun.* **2012**, *48*, 5013–5015.
- (17) Cognigni, A.; Gaertner, P.; Zirbs, R.; Peterlik, H.; Prochazka, K.; Schröder, C.; Bica, K. *Phys. Chem. Chem. Phys.* **2016**, *18*, 13375.
- (18) Vasiloiu, M.; Gaertner, P.; Zirbs, R.; Bica, K. *Eur. J. Org. Chem.* **2015**, *2015*, 2374–2381.
- (19) Cokoja, M.; Reich, R. M.; Wilhelm, M. E.; Kaposi, M.; Schäffer, J. D.; Morris, S.; Münchmeyer, C. J.; Anthofer, M. H.; Markovits, I. I. E.; Kühn, F. E.; Herrmann, W. A.; Jess, A.; Love, J. B. *ChemSusChem* **2016**, *9*, 1773–1776.
- (20) Łuczak, J.; Jungnickel, C.; Markiewicz, M.; Hupka, J. *J. Phys. Chem. B* **2013**, *117*, S653–S658.
- (21) Ressmann, A. K.; Zirbs, R.; Pressler, M.; Gaertner, P.; Bica, K. Z. *Naturforsch., B: J. Chem. Sci.* **2013**, *68*, 1029–1037.
- (22) Moniruzzaman, M.; Kamiya, N.; Nakashima, K.; Goto, M. *Green Chem.* **2008**, *10*, 497–500.
- (23) Ventura, S. P. M.; Santos, L. D. F.; Saraiva, J. A.; Coutinho, J. A. P. *Green Chem.* **2012**, *14*, 1620–1625.
- (24) *Ionic Liquid-Based Surfactant Science: Formulation, Characterization, and Applications*; Paul, B. K., Moulik, S. P., Eds.; Wiley: Hoboken, NJ, 2015.
- (25) Hecht, S. E.; Cron, S. L.; Scheibel, J. J.; Miracle, G. S.; Seddon, K. R.; Earle, M.; Gunaratne, H. Q. N. Ionic liquids derived from functionalized anionic surfactants. World Patent 2006050312, 2006.
- (26) Collins, I. R.; Earle, M. J.; Exton, S. P.; Plechkova, N. V.; Seddon, K. R. Ionic liquids, making emulsion containing ionic salt, and surfactant uses. WO Patent 2006 111712, 2006.
- (27) Anderson, K.; Fanselow, M.; Holbrey, J. D. Method for separating emulsions. World Patent WO 2006 131699, 2006.
- (28) Bowlas, C. J.; Bruce, D. W.; Seddon, K. R. *Chem. Commun.* **1996**, 1625–1626.
- (29) Robertson, A. J.; Seddon, K. R. Preparation of phosphonium phosphinate compounds for use as polar solvents. World Patent WO 02 079212, 2002.
- (30) Gayet, F.; El Kalamouni, C.; Lavedan, P.; Marty, J.-D.; Brûlet, A.; Lauth-de Viguerie, N. *Langmuir* **2009**, *25*, 9741–9750.
- (31) Li, N.; Gao, Y. a.; Zheng, L.; Zhang, J.; Yu, L.; Li, X. *Langmuir* **2007**, *23*, 1091–1097.
- (32) Qiu, Z.; Texter, J. *Curr. Opin. Colloid Interface Sci.* **2008**, *13*, 252–262.
- (33) Winsor, P. *Trans. Faraday Soc.* **1948**, *44*, 376–398.
- (34) Clauss, M.; Peyrelasse, J.; Heil, J.; Boned, C.; Lagourette, B. *Nature* **1981**, *293*, 636–638.
- (35) Rojas, O.; Tiersch, B.; Frasca, S.; Wollenberger, U.; Koetz, J. *Colloids Surf., A* **2010**, *369*, 82–87.
- (36) *Handbook of Organopalladium Chemistry for Organic Synthesis* (2 Vol. Set); Negishi, E. I., de Meijere, A., Eds.; Wiley-Interscience: New York, 2003.
- (37) Mathews, C. J.; Smith, P. J.; Welton, T. *Chem. Commun.* **2000**, 1249–1250.
- (38) Lennox, A. J. J.; Lloyd-Jones, G. C. *Chem. Soc. Rev.* **2014**, *43*, 412–443.
- (39) Nowothnick, H.; Blum, J.; Schomäcker, R. *Angew. Chem., Int. Ed.* **2011**, *50*, 1918–1921.
- (40) Atkins, M. P.; Seddon, K. R.; Swadźba-Kwaśny, M. *Pure Appl. Chem.* **2011**, *83*, 1391–1406.
- (41) Reisinger, C. M.; Nowack, R. J.; Volkmer, D.; Rieger, B. *Dalton Trans.* **2007**, 272–278.
- (42) Schuster, O.; Yang, L. R.; Raubenheimer, H. G.; Albrecht, M. *Chem. Rev.* **2009**, *109*, 3445–3478.
- (43) Hollóczki, O.; Gerhard, D.; Massone, K.; Szarvas, L.; Németh, B.; Veszprémi, T.; Nyulászi, L. *New J. Chem.* **2010**, *34*, 3004–3009.
- (44) Budroni, G.; Corma, A.; García, H.; Primo, A. *J. Catal.* **2007**, *251*, 345–353.
- (45) Singh, A. S.; Shelkar, R. S.; Nagarkar, J. M. *Catal. Lett.* **2015**, *145*, 723–730.
- (46) Astruc, D. *Inorg. Chem.* **2007**, *46*, 1884–1894.
- (47) Behr, A.; Henze, G.; Johnen, L.; Awungacha, C. J. *Mol. Catal. A: Chem.* **2008**, *285*, 20–28.
- (48) Gilmore, B. F.; Andrews, G. P.; Borberly, G.; Earle, M. J.; Gilea, M. A.; Gorman, S. P.; Lowry, A. F.; McLaughlin, M.; Seddon, K. R. *New J. Chem.* **2013**, *37*, 873–876.
- (49) Avent, A. G.; Chaloner, P. A.; Day, M. P.; Seddon, K. R.; Welton, T. *J. Chem. Soc., Dalton Trans.* **1994**, 3405–3413.